

# Tunable Self-assembly of Au-nanoparticles with Near-Perfect Monodispersity

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## Abstract

Au nanoparticles with near perfect monodispersity in shape and size self-assemble, very slowly and at room temperature, on polystyrene films for film thickness  $\leq 4R_g$ ,  $R_g$  being unperturbed polymer gyration radius. Nanoparticle shape and size can be tuned, without sacrificing monodispersity, by changing polymer film thickness. Self-assembly is caused by enhanced two-dimensional diffusion of sputter-deposited Au clusters on a distribution of surface energy variations, sharply defined and with tunable dimensions, corresponding to low cohesion between gyration spheres on film surface. Lowering of cohesion and enhanced surface diffusion are clearly related to confinement-induced gyration sphere layering along film depth.

The fundamental aspect of nanoparticles is the emergence of totally new structures and properties that are crucially dependent on the size and shape of the nanoparticles [1, 2]. Hence a system of nanoparticles has well-defined structure and properties only when it is monodisperse, i.e., when all nanoparticles in the system have the same size and shape. For metal nanoparticles this means that each particle has a sharply defined number of metal atoms arranged in a specific way, which, when changed to some other arrangement, gives a new well-defined system of nanoparticles. Nanoparticles are thus different from both the bulk solid, where the number of atoms is indefinite, and the molecule, where it is unchangeable. The prevalent methods of producing nanoparticles are thus either ‘top-down’ or ‘bottom-up’. In the first, nanosized pieces are broken off the bulk [3, 4, 5] and deposited on a substrate. In the second, nanoclusters of specific atoms are assembled using specific chemical interactions [6, 7, 8]. However, both methods have inherent problems. In the first, or physical, method it is easy to tune the number of atoms and their arrangements in the nanoparticle by changing the energy of collision and / or the crystal face of the bulk but the system produced is generally not monodisperse [9]. This is due to the inherent energy-width of the projectile-solid interactions that determine the morphology of nanoparticles grown from these projectile clusters[10]. In the second, or chemical, method remarkable monodispersity is achieved due to specificity of chemical reaction [11, 12] but this very specificity makes changing the nanoparticle shape and size nearly impossible and generalized chemical methods for growing nanoparticles is the focus of recent research[13, 14].

A nanoparticle can be viewed also as a cluster of atoms of a specific number and arrangement, which is in metastable equilibrium [1]. In other words, nanoparticles correspond to local minima in free energy as functions of the cluster shape and size and, if suitable ‘potential wells’ are provided, atomic clusters will most probably occupy them, thus forming well-defined nanoparticles. Changing the depth and width of such ‘potential wells’ would then change the shape and size of the nanoparticle and would, at each case, sharply choose a particular shape and size, preserving monodispersity. This concept forms the basis of another mode of producing nanoparticles, that of *tunable self-assembly*.

In this communication we have presented a realization of such tunable self-assembly of Au nanoparticles sputter-deposited on a spin-coated polystyrene (*PS*) film on amorphous quartz. We have found that, reducing thickness of the *PS* film reduces adhesion of the initially deposited Au, resulting in an enhanced ambient surface diffusion of initially formed

Au clusters - a slow two-dimensional Brownian motion over a surface layer having effective viscosity at room temperature orders of magnitude lower than bulk PS viscosity near glass transition temperature ( $T_G \simeq 100^\circ\text{C}$ )[15]. At the same time we find that the film makes the clusters form larger nanoparticles with near-perfect monodispersity in size and shape that can be tuned by changing film thickness within a range, without sacrificing the monodispersity. We have found that the formation of nanoparticles with fixed size and shape is achieved by trapping the clusters in sharply defined surface energy gradients ('wells') with fixed dimensions, appearing on *PS* film surface whose dimensions decrease with increase in film thickness.

Polystyrene (mol. wt.  $M \simeq 560900$ , unperturbed radius of gyration  $R_g = 0.272M^{\frac{1}{2}} \simeq 20.4\text{nm}$ ) [16] was spin-coated on fused quartz from toluene solutions to form films with air/film and film/substrate interfacial roughness  $\sim 0.6\text{nm}$ . The thickness was controlled by a combination of rotation speed and solution concentration and varied from 40 nm ( $\simeq 2R_g$ ) to 180 nm ( $\simeq 9R_g$ ). A series of these *PS* films was used as the pristine (*pPS*) samples while Au was D.C. sputter-coated for 10s [19] on a second identical series forming the *AuPS* samples.

Figure 1((a)-(c)) show the topographic images of Au-nanoclusters, obtained from tapping mode Atomic Force Microscopy (AFM), immediately after sputter deposition on a *PS* film of thickness  $d \simeq 2R_g$  (Figure 1(a)), and after two months (Figure 1(b)) and six months post-deposition (Figure 1(c)) all taken at room temperature. While the first image shows no cluster-like features, combination of results from the plasmon peak in transmission optical spectra [17] and the electron density profile (EDP) (top inset, Figure 1(a)) extracted from x-ray reflectivity (bottom inset, Figure 1(a))[18] confirms the presence of a layer of spherical Au clusters with diameter  $\simeq 3$  nm only on top of the *PS* films (top inset and bottom inset of Figure 1(a) are not shown). The image taken after two months, on the other hand, shows presence of larger and ellipsoidal nanoparticles as indicated by in-plane semi-axes,  $a$  and  $b$  and out-of-plane semi-axis  $c$  ( $a \approx b > c$ ) (Table 1), whereas in Figure 1(c) there is almost no change in these dimensions suggesting that growth of the particles has stopped. From the values of  $a$ ,  $b$  and  $c$  over time (Table 1) it is clear that initial small and spherical nanoparticles are coalescing, predominantly in-plane and at room temperature, to form larger and ellipsoidal nanoparticles.

Figures 1(d) and 1(e) show the images taken just after and two months after Au de-

position, respectively, on  $d \simeq 4R_g$  *PS* film and Figures 1(f) and 1(g) show the same time sequence for the  $d \simeq 9R_g$  film. Au was deposited and kept under conditions identical with  $d \simeq 2R_g$  film. Coalescence of particles is again observed in the  $4R_g$  thick film with some modifications (Table 1) but there is almost no coalescence in the  $9R_g$  thick *PS* film.

The lower panel of Figure 1 show the reflectivity profiles of *pPS* films of  $d \simeq 2R_g$  (Figure 1(h)),  $d \simeq 4R_g$  (Figure 1(i)) and  $d \simeq 6R_g$  or 120nm (Figure 1(j)). In each case the reflectivity data is shown by open circles while the calculated best fit is shown by solid line and the extracted EDP is shown in inset. As expected [20], below  $d \simeq 4R_g$ , *PS* molecules form layers along film thickness with periodicity  $\sim R_g$ . The key point is to note that this layer formation is strongly correlated with surface coalescence of Au nanoparticles. (For Figure 1(h), (i), (j) see [20]: Fig 3(a) and 3(b))

Figure 2 presents the monodispersity of the self-assembled nanoparticles. Figure 2(a) and 2(b) show, respectively, topographic and phase images of Au-nanoparticles formed on the  $2R_g$  thick *PS* film two months after deposition, while Figure 2(c) presents (in filled circles)  $N$ , the number of nanoparticles with a particular value of  $a(\simeq b)$  as a function of  $a$ . We have averaged over four  $2\mu\text{m} \times 2\mu\text{m}$  scans. The size distribution in our case is completely different and much sharper than the log-normal distribution of sizes of nanoparticles formed by random coalescence [21]. This precludes any random coalescence mechanism such as the Vollmer-Weber growth [22] and it strongly suggests presence of potential wells with fixed depth and width that act as size-selective traps for the Au-nanoparticles to fall into and form the larger nanoparticles. We have also found that this monodispersity is not disturbed for  $d \leq 4R_g$ .

Figures 3(a), 3(b), and 3(c) show the topographical and Figures 3(d), 3(e) and 3(f) show the phase image of *pPS* films of  $d = 2R_g$ ,  $4R_g$  and  $9R_g$ , respectively. All the topographical images look the same, having roughly spherical features with an average diameter of  $R_g$ , as seen previously [20] and shown, for example, in the line profile (inset, Figure 3(b)(not shown)), clearly indicating the presence of gyration spheres in *pPS* films at all thickness with a size modification probably due to entanglement and substrate effects. On the other hand the phase images exhibit larger changes in phase-shifts between adjacent ‘spheres’ as the thickness is reduced, implying a larger change in energy being dissipated by the AFM tip in going over from one sphere to another[23]. We have estimated this average energy

dissipated by the tip over the film surfaces, using the expression [24]

$$\sin \phi = \left( \frac{\omega}{\omega_0} \frac{A}{A_0} \right) + \frac{QE_D}{\pi k A A_0} \quad (1)$$

where  $\phi$  is the phase-shift,  $\omega$  ( $\omega_0$ ) is the working (resonance) frequency,  $A$  ( $A_0$ ) is the setpoint (free) amplitude,  $Q$  is the quality factor, and  $k$  is the cantilever spring constant while  $E_D$  is the energy dissipation.

The average energy dissipated per unit tip-sample contact area is then given by [16]

$$W_D = \frac{E_D}{4\pi a_{Si} r_c} \quad (2)$$

where  $r_c$  = radius of tip-curvature,  $a_{Si}$  = diameter of Si atom of tip. The surface energy ( $\gamma_{PS}$ ) of the polymer film is then given in terms of the interfacial energy ( $\gamma_{Si-PS}$ ) and the Si surface energy ( $\gamma_{Si}$ ) as [16]

$$\gamma_{Si-PS} = -\frac{W_D}{2} = (\gamma_{Si}^{\frac{1}{2}} - \gamma_{PS}^{\frac{1}{2}})^2 \quad (3)$$

We have obtained average  $\gamma_{PS} \simeq 30 \text{ mJm}^{-2}$ , consistent with bulk polystyrene values ( $\simeq 33 \text{ mJm}^{-2}$ ) [16]. In Figures 3(g), 3(h), 3(i), we have shown  $\Delta\gamma_{PS}(x, y)$ , the surface energy relative to top of the gyration spheres, derived from Figure 3(d), 3(e) and 3(f), respectively (Figure 3(a), (b), (c), (d), (e), (f), (g), (h), (i) are not shown, Figure 3(j) corresponds to them). Variation in surface energy, i.e. magnitude of  $\Delta\gamma_{PS}(x, y)$  between adjacent gyration spheres increases as film thickness is reduced, indicating the ‘disentanglement’ of the spheres due to decrease in cohesion. Typical line profiles ( $\Delta\gamma_{PS}(x)$ ) across such variations presented in Figure 3(j) show a decrease in surface energy on top of spheres relative to their contact region. For non-H-bonding solids and liquids the Hamaker constant,  $A_H \approx 2.1 \times 10^{-21} \gamma$  ( $\gamma$  in  $\text{mJm}^{-2}$  and  $A_H$  is in Joules). The decrease in Hamaker constant ( $\Delta A_H$ ) between the top and bottom of the line profiles, i.e., between contact region of adjacent gyration spheres and top of spheres, obtained from the above expression, are given in Table 1. They match values of the decrease in Hamaker constant between molecular layers, formed by confinement, along depth, in films of the corresponding thickness [20], also presented in Table 1. Thus confinement lowers cohesion between adjacent gyration spheres, ie, molecules of *PS*, both parallel and perpendicular to the direction of confinement. The decreasing variation in surface energy with increasing film thickness is clearly consistent with the decreasing dimensions of the coalesced nanoparticles (Table 1) and final stopping of coalescence. This suggests that the

driving mechanism of the coalescence is the sharply defined in-plane gradients in surface energy.

In the case of lowering of cohesion across the film thickness, we showed that this lowering is associated with breakdown of intermolecular excitonic coupling through J-interaction between adjacent benzene rings [20]. If we assume that the same mechanism to be active along the film plane, we would expect consequent changes in the in-plane properties such as visco-elasticity.

$T_G$  of bulk *PS*, or even its surface ( $\simeq 77^\circ\text{C}$ )[15], is much above room temperature. The fact that Au nanoparticles are still diffusing on *PS* surface, albeit slowly, attests to low Au-*PS* adhesion [25]. Therefore two-dimensional Brownian motion is the preferred mechanism of diffusion [26]. It is also known that, near  $T_G$ , there is a ‘liquid-like’ surface layer of thickness  $\sim 4\text{nm}$  for polymers in general [27] on which surface diffusion of clusters has been found to be orders of magnitude faster than bulk diffusion [22]. If we assume a two-dimensional Brownian motion even at ambient conditions, for the initially deposited Au clusters, we can estimate the effective viscosity of the ‘liquid’ surface layer of the film at room temperature. We have used the Smoluchowski relation [28]

$$\eta = \frac{4k_B T t}{6\pi \langle r^2 \rangle a_D} \quad (4)$$

where  $\langle r^2 \rangle^{\frac{1}{2}} =$  distance traversed by diffusing Au cluster in time  $t$ ,  $a_D =$  cluster radius,  $\eta =$  effective viscosity of surface ‘liquid’ layer at temperature  $T$  and  $k_B =$  Boltzmann constant. If we take  $2a_D \simeq 3\text{ nm}$ ,  $\langle r^2 \rangle^{\frac{1}{2}} =$  radius of *pPS* gyration sphere measured from Figure 3(FWHM of line profile)  $\sim R_g/2 = 9\text{ nm}$ , we arrive at  $\eta = 3.71 \times 10^{11}$  Poise for  $d \simeq 2R_g$  at room temperature, which is two order of magnitude less than  $\eta_{bulk}$  for *PS* (at  $T_G$ ) [29] (Table 1). For  $d \simeq 4R_g$  the value is of the same order but for  $d \simeq 9R_g$ , as there is almost no coalescence, the surface behaves essentially like bulk *PS* at room temperature. The large decrease in surface viscosity due to confinement strongly suggests a compositional change on the surface of gyration spheres of *PS*, accounting for both the lowering of cohesion and Au-*PS* adhesion (causing enhanced effective viscosity). In Figure 3(k) we have shown plasmon peaks of Au nanoparticles, just after deposition, on *PS* with  $d \simeq 2R_g$  and  $4R_g$  (Figure 3(k) is not shown). Under identical deposition conditions, the peak at 580 nm, corresponding to individual nanoparticle, is seen to be reduced while the other (non-gaussian) peak, corresponding to inter-nanoparticle coupling [30], is absent for the thinner film. This indicates that lesser

amount of Au adhere to the surface of the thinner film, to begin with [31] and it also explains why fewer nanoparticles are formed in this case.

No chemical reactions could possibly have taken place while thinning. Also we know that thinning breaks the intermolecular benzene-benzene connection [20]. We then suggest that a probable mechanism for all the observed effects is a rearrangement on surfaces of the gyration spheres [32] whereby the proportion of benzene rings on these surfaces is reduced with respect to that in bulk *PS*. The lower Au-methylene adhesion, as compared to Au-benzene adhesion causes faster diffusion of the Au clusters. Due to lack of benzene rings, the J-coupling between spheres also reduces, lowering cohesion between adjacent spheres and forming gradients in surface energy that trap the diffusing nanoclusters to form monodisperse nanoparticles.

The confinement-induced tuning of surface energy described above is more generalized than chemically controlling surface energy [33]. The biggest advantage of using polymers in the growth of nanoparticles, which is essentially a phenomenon at mesoscopic lengthscales, is that the molecules of a polymer are themselves objects at such lengthscales. Thus molecular rearrangements at polymer surfaces can, as in our case, be employed to direct nanoparticle growth. However, such rearrangements can also cause very interesting changes in other surface properties at mesoscales, eg, optical polarization as a function of film thickness. Work in these directions is underway. (Some figures are described but not shown here due to insufficient space in arXiv).

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## Figure captions

FIG. 1: (a)-(g): Topographic images of ( $500nm \times 500nm$ ) Atomic Force Microscopic (AFM) scans in tapping mode (intermittent contact) of Au sputter deposited on polystyrene (*PS*) films. Thickness, in units of  $R_g$ = unperturbed *PS* gyration radius ( $\simeq 20.4nm$ ), and time lapsed after Au deposition given in pairs. (a)  $2R_g$ , immediate; (b)  $2R_g$ , 2 months; (c)  $2R_g$ , 6 months; (d)  $4R_g$ , immediate; (e)  $4R_g$ , 2 months; (f)  $9R_g$ , immediate; (g)  $9R_g$ , 2 months. Observed (open red circles) and best fit (black line) x-ray reflectivity profile and Electron Density Profile (EDP) extracted from fit for the corresponding Au-*PS* film are shown, bottom and top insets of (a), respectively. (h)-(j): Reflectivity profiles, observed (open red circles) and calculated (black lines) with EDP's extracted from calculated profiles (insets) for pristine *PS* films with thickness (i)  $2R_g$ , (j)  $4R_g$ , (k)  $9R_g$ .

FIG. 2: (a) Topographic and (b) Phase images of ( $2\mu m \times 2\mu m$ ) AFM scans of Au nanoparticles formed on  $2R_g$  thick PS film 2 months after Au deposition. (c)  $N$  vs  $a$  plot (in filled circles),  $a(\simeq b)$  is the in-plane semi-major axis of the nanoparticles in (a) and (b) and  $N$  is the number of nanoparticles with particular value of  $a$ .

FIG. 3: (a)-(c): Topographic and (d)-(f): Phase images of ( $500nm \times 500nm$ ) AFM scans of pristine *PS* films with thickness  $2R_g$  ((a) and (d)),  $4R_g$  ((b) and (e)) and  $9R_g$  ((c) and (f)). Inset (b): line profile along a gyration sphere. (g)-(i): In-plane maps of  $\Delta\gamma_{PS}$ , surface energy relative to top of the gyration spheres (shown in (a)-(c), respectively, refer text for details). (j):  $\Delta\gamma_{PS}$ , plotted along typical lines in (a), (b) and (c), across adjacent gyration spheres given by curves 1, 2 and 3, respectively. (k): Plasmon peaks in optical transmission spectra of Au-*PS* films, just after Au deposition for *PS* thickness (1)  $2R_g$  and (2)  $4R_g$ .

TABLE I: Structure of Au nanoparticles and visco-elasticity of polystyrene films

| <i>PS</i><br>film<br>thickness<br>(nm) | Au nanoparticle<br>dimension (nm) |          |          |                             |          |          | In-plane<br>Hamaker constant<br>variation ( $\Delta A_H$ )<br>(meV) | Interlayer<br>Hamaker constant<br>variation ( $\Delta A_H$ ) <sup>c</sup><br>(meV) | Effective<br>surface<br>viscosity of <i>PS</i><br>$\eta$ , (Poise) | Bulk<br>viscosity<br>of <i>PS</i> <sup>d</sup><br>$\eta_{bulk}$ , (Poise) |
|--|-----------------------------------|----------|----------|-----------------------------|----------|----------|---|--|--|---|
|  | as deposited <sup>a</sup>         |          |          | after 2 months <sup>b</sup> |          |          |   |  |  |   |
|  | <i>a</i>                          | <i>b</i> | <i>c</i> | <i>a</i>                    | <i>b</i> | <i>c</i> |   |  |  |   |
| $2R_g$                                 | 3                                 | 3        | 3        | 26                          | 26       | 6        | 63  | 97   | $\sim 3.71 \times 10^{11}$   | $\sim 10^{13}$  |
| $4R_g$                                 | 3                                 | 3        | 3        | 10                          | 10       | 3        | 15  | 28   | $\sim 3.71 \times 10^{11}$   |   |
| $9R_g$                                 | 3                                 | 3        | 3        | 3                           | 3        | 3        | 8   | $\sim 0$   | -  |   |

<sup>a</sup>From plasmon spectra and x-ray reflectivity

<sup>b</sup>From spectra, AFM and x-ray reflectivity

<sup>c</sup>From [20]

<sup>d</sup>Above  $T_G$ , from [29]